

ES-65-DIV-8
09/752,894

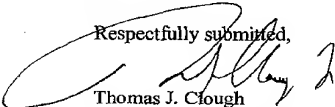
REMARKS/ARGUMENTS

Applicant expresses his appreciation for the telephone communication from the Examiner on December 4, 2003. Applicant has rewritten paragraph 1 on page1 of the specification to encompass the previous claims for priority to the earlier filed applications. Further, applicant has amended the claims as per the Examiner's recommendation to delete the referenced numbers in claims 7 and 8, to correct the dependency of claim12 and to revise claims 1, 9 and 16 to the previously presented format.

In conclusion Applicant submits that the present claims are patentable and allowable and respectfully requests the Examiner to forward this application to issuance at an early date.

Should any matters remain unresolved, the Examiner is requested to call (collect) Applicant's attorney at the numbers given below.

Respectfully submitted,


Thomas J. Clough
Registration No. 22337
Attorney for Applicant
P.O. Box 718
Pismo Beach, California 93448
(805) 481-3750
Facsimile (805) 481-3452

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to Commissioner of Patents and Trademarks, Washington, D.C. 29231 on or before Dec 5, 2003.

Dated this 5th day of Dec., 2003.


Thomas J. Clough, Attorney

PROCESS FOR REDUCING THE PARTICLE SIZE OF POROUS ORGANIC
POLYMERS AND PRODUCTS PRODUCED THEREFROM

Related Applications

This application is a continuation in part of application of application Serial Number 08/674,404, filed July 2, 1996. This earlier filed application is incorporated in its entirety herein by reference.

Background of the Invention

The present invention relates to a process for reducing the mean particle size of resilient porous organic polymer particles having open cell pores which resist particle size reduction due to the compressibility and resiliency of the organic polymer. Further, the present invention relates to novel products produced by the process for reducing the mean particle size and to particles of reduced mean particle size which have a functional release additive contained in the pores thereof.

The present invention further relates to an improved lead acid battery element containing metal impurity inhibiting porous polymeric additives which are added to the positive active material, negative active material and/or battery separator to inhibit the detrimental effects of certain metals on the efficiency of a lead acid battery, particularly the negative plate battery element and to polymeric macroporous additives that enhance active material utilization efficiency and improvement in the utilization of sulfuric acid electrolyte necessary for the discharge reaction of a lead acid battery which are produced by the process of this invention.

Resilient porous organic polymers resist permanent deformation and have been found to be difficult to process, if at all, for size reduction in conventional grinding processes. Conventional grinding processes are typically used to grind and produce particle size reduction for solid type particles which have little or no compressibility and which can vary in particle hardness. Typical grinding processes such as universal mills, slurry mills, fluid energy mills, cone mills and hammer mills are generally effective for such solid type particles, particularly brittle type particles. One of the problems with the use of conventional grinding mills for size reduction of resilient porous organic polymers is that the particles compress under the applied forces, i.e., the particles are compressible and regain substantially the same geometry when the force is removed. Unlike solid particles particularly, brittle particles, the conventual grinding mill approaches used for dry solid particles produces substantially less or even no size reduction of resilient porous polymers in the dry powder form. Further, attrition type grinding mills have had little overall effectiveness when the organic polymers were incorporated into a liquid slurry.

In many applications that use porous organic polymers as additives such as the use of additives in lead acid batteries, it is preferred to have a non-spherical geometry such as an elongated geometry and/or a geometry that has a length to diameter which is greater than one, in order to provide improved overall performance of the additive. It is therefore desirable to produce porous organic particles of reduced size by processes which produce a non-spherical geometry.

Thus, for the many applications in which porous organic polymers are used, particularly there use as additives, wherein a reduced particle size and/or particle size

distribution offers performance advantages, there is a need for a process which is effective for reducing the particle size of resilient porous organic particles at reasonable process conditions and processing times, particularly processing conditions at atmospheric pressure and ambient temperatures at preferably commercial scale processing times.

Summary of the Invention

A new process for reducing the mean particle size of resilient porous organic polymer particles having open cell pores has been discovered. In brief, the process includes the steps of forming an aqueous particle slurry comprising a major amount of water, both internal and external to the particles and a ~~minimum~~ ^{minor} amount of particles to form a slurry and subjecting the aqueous slurry to a cutting action by contact with a plurality ~~polarity~~ of cutting surfaces to reduce the mean particle size of the particles and recovering particles of reduced mean particle size.

New porous organic polymers of reduced particle size produced by the cutting process have also been discovered. In brief, the new products produced by the process have a non-spherical geometry, typically elongated and/or a length to diameter to width aspect ratio greater than one. The products find use as additives in lead acid battery elements and in polymer coatings, films and composites when used as a functional additive release agent or additive.

A new battery element which inhibits the detrimental effect of soluble metal impurity on the negative plate has been discovered. In brief, the battery elements include the addition of a porous organic polymer produced by the process of this invention having functional groups with a preferential affinity for the metal impurity in the cation

or anion state, to the positive active material, the negative active material or the separator which separates the positive and negative plates within a lead acid battery and which typically is a reservoir for sulfuric acid electrolyte.

A new battery element which improves utilization efficiency of the active material in a lead acid battery has been discovered. In brief, the battery elements include the addition of macroporous containing organic particle additives produced by the process of this invention to the active material in the positive or negative plates of a lead acid battery to improve overall utilization efficiency and the utilization of sulfuric acid electrolyte during discharge of the battery.

Detailed Description of the Invention

In one broad aspect, the present process reduces the mean particle size of resilient porous organic polymer particles having open cell pores comprising the steps of forming and aqueous particle slurry comprising a major amount of water and a minor amount of said organic polymer particles wherein said water is present in a least a part of the internal pores of the particles to provide a degree of resistance to particle compressibility and in addition, external to said particles to form a slurry. The slurry is subjected to a cutting action by contact with a plurality of cutting surfaces to reduce the mean particle size of the particles. The particles of reduced mean particle size are then recovered typically using conventional separation processes.

The porous organic polymer particles typically have open cell pores, i.e., pores that are interconnected and

open to the outer surface, and are resilient, i.e., the particles can be compressed and resist permanent deformation under low or even moderate forces of compression. Typically, the porous organic particles have at least about 40% porosity, more typically, at least about 60% porosity, i.e., the volume of the pores represent such percentage of the total volume of the particles typically from the standpoint of the average mean percent porosity of the particles. The average mean pore size distribution of the particles can vary over a wide range, typically varying from about 0.02 microns to about 15 microns, more typically, from about 0.03 microns to about 12 microns and still more typically from about 0.75 microns to about 10 microns. The organic porous particles prior to size reduction typically have an average mean particle-diameter of greater than about 2,000 microns, typically greater than about 1,000 microns, although, particles having an average mean diameter greater than 400 microns can be processed within the process of this invention. Particles produced by the process of this invention have a reduced mean particle size typically less than about 200 microns, more typically less than about 150 microns and still more typically less than about 100 microns.

The chemical composition of the porous organic polymers can vary widely and include polyolefins, such as polypropylene and polyethylene, nylons and the like. One of the substantial advantages of the process of this invention is that porous organic polymers which are hydrophobic, i.e., not significantly water wet, can be processed according to the process of this invention to reduce the average mean particle size of the porous particles.

In the process of this invention, the porous organic polymer particles are combined with a major amount of water to form an aqueous particle slurry. As set forth above, the porous organic polymers have open cell porosity which allows water to be present in at least a part of the internal pores of said particles. It has been found that the presence of such water provides resistance to particle compressibility and enhances the effect of a cutting action to reduce the mean particle size of the porous particles. Typically, water will occupy at least about 10% more preferably at least about 50% of the pore volume of the particles or even greater than about 85% of the volume of the pores within said particles. It is preferred to have water present in the internal pores at a percent of the volume of the internal pores which enhance the resistance to particle compressibility and in addition which aids in the formation of an aqueous particle slurry, i.e., produces a higher density particle.

The aqueous particle slurry comprises a major amount of water said major amount of water being that water which is part of the internal pores of the particles and also that water which is external to said particles to form a slurry. Typically, the combined internal and external water represents at least about 80% of the total weight of the slurry, i.e., water and particles, i.e., the weight of particles on a dry basis, typically greater than about 85% and more typically and preferred greater than about 90wt% basis the total weight of the slurry.

The aqueous particle slurry can be formed by combining porous organic polymers, typically in a dry form, with water under mixing conditions. Depending on the pore volume of the organic porous polymers, the density of the porous

polymers can be significantly less than water such as less than 0.5gm per cc. In order to enhance the presence of water in the internal pores of the porous particles, a vacuum can be applied, with mixing, to aid in wetting out of the porous polymers. In addition and particularly when the organic polymers have hydrophobic character, a small amount of a surfactant, such as a non-ionic surfactant, can be added to the aqueous slurry to enhance wetting out of the internal surfaces of the pores of the particles and the presence of water within the internal pores. The use of surfactants such as hydrocarbon or fluorosurfactants to assist in such wetting of polymer surfaces are well within the skill of the art.

The aqueous particle slurry is subjected to a cutting action by contact with a plurality of cutting surfaces to reduce the mean particle size of the particles. As set forth above, the porous organic particles are resilient. The term resilient refers to particle compressibility when subjected to an external force or pressure at the process conditions of temperature and pressure when the particles are subjected to the cutting action at the cutting surface. Thus, for example, the temperature of the particles may increase at the cutting surface as heat is generated during the cutting action. The term resilient refers to the condition of the particles under the conditions of temperature and pressure when the particles are in contact with the cutting surface. In one embodiment of the process of this invention the liquid particle slurry is fed to the center of a high speed rotating impeller. Centrifugal forces then move the particles outward to cutting surfaces where the particles pass through the cutting edges of a stationary cutting head. The cutting action reduces the

average mean particle size of the porous organic particles. It is preferred that the cutting surfaces be stationary with the slurry being fed to a rotating non-cutting slurry distribution means, such as a rotating
5 impeller. The term rotating cutting action includes those processes wherein the cutting surfaces are stationary.

One of the substantial advantages of the process of this invention is that difficulty to process resilient porous organic polymers for size reduction can be processed
10 and achieve size reduction typically at relatively short residence times, i.e., the porous organic polymers are in contact with the cutting surfaces typically less than 15 seconds, more typically, less than 5 seconds and even more typically less than 1 second. One of the further advantages
15 of the process of this invention is the ability to produce non-spherical particles of reduced average mean particle size. As set forth above, many additive type applications have a preference for non-spherical geometry's, i.e., one or more of the dimensions of length, width and thickness, i.e.,
20 height are different. The process of this invention can produce non-spherical porous polymer particles of reduced average mean size having varying length to width to height ratios, i.e., the particles can be elongated and non-spherical.

25 The porous organic polymer particles after size reduction can be recovered by conventional processes. Typical examples of such recovery processes are filtration, such as rotary and vacuum filters, screens such as vibrating screens and centrifuges. The choice of the
30 recovery process can be varied depending on the end use application of the recovered particles. For example, a typical additive for use in lead acid batteries may have an

acceptable moisture content of from about 40 to 60 wt%. In other end use applications substantial or complete dewatering of the internal pores may be required. The above recovery processes typically remove about 90%, typically greater than 95% of the external water that forms the aqueous particle slurry. *and can produce a dry free flowing particle.* The percentage of the internal water removed will vary according to the end use application. It is contemplated within the scope of this invention that there can be substantial dewatering of the internal pores including dewatering of from about 85 to about 100%, more typically from about 90 to 100% of the internal water, i.e., less than about 10wt% moisture. As set forth above, the degree of the dewatering of the internal pores relates to the final end use application of the particle products. *Yp 10/6/03*

As is recognized by those of skill in the art, a number of the above recovery processes have the capability to recover particles of different size classifications. Thus for example, the product might be recovered at a certain top size, for example less than about 150 microns or less than about 100 microns with the larger materials not within that size classifications being recovered and further processed to achieve a given size classification. The larger particles can be recycled and combined with the incoming slurry for purposes of efficiency and cost effective processing. However, particle size distribution and cut off upper and lower limits, in general, is a function of the end use applications and the specifications set by those applications for particle size distribution.

As set forth above, the porous polymers can be reloaded with liquid additives including meltable solids by mixing the organic porous polymers of reduced particle size with

the liquid additive. The porous structure typically acts like tiny sponges with the ability to absorb such liquids typically up to several times their own weight. It is believed that the pores of the porous polymers are filled by capillary absorption. After the liquid additive is added to the porous polymer, the system generally remains dry and free-flowing. In order to maximize the absorption of the liquid additive, it is preferred that the internal water be substantially removed from the porous polymer prior to addition of the liquid additive. The loaded porous polymers can then be used in many applications and combined with other polymer to provide an additive concentrate as a free-flowing powder. Typical low melting additives which can be incorporated into the porous polymers are anti-static agents, slip / anti-block agents, mould release / permanent lubricants, anti-fog agents, antioxidants, light stabilizers, nucleating agents, peroxides, biocides, fragrances, insecticides, pharmaceuticals, agricultural agents, pheromones and the like. As is known by those of skill in the art, that the additives themselves may be liquid or if solid, can be added to a liquid carrier such as an organic or water based carrier in which the additive is dissolved, emulsified and/or dispersed in order for the additive and carrier to be absorbed in the pores of the polymer. The pore diameter of the polymer is generally selected in order to achieve a rapid uptake of the liquid additive material and which also produces, in general, a dry and free-flowing powder. Typically, loading capacities greater than 50% or even up to 70% or more can be loaded with the liquid additive.

In another broad aspect, the present battery elements comprise the addition of an organic polymer containing

functional groups with a preferential affinity for metal impurity in the cation or anion state to the positive active material, the negative active material and/or the separator which separates the positive plates from the negative plates in a lead acid battery. In a preferred embodiment, the organic polymers are porous, i.e. the porosity of the polymer allows the soluble metal impurity in the electrolyte to contact both the outer surface of the polymers and the internal surfaces created by the porosity of the organic polymers, particularly porous polymers produced by the process of this invention. The functional groups having a preferential affinity for metal impurity include both functional groups on the outer surface and internal surfaces in contact with soluble metal impurity in the electrolyte. The metal impurity inhibiting additives are typically incorporated into the negative active material, the positive active material and/or the separator in an amount sufficient to inhibit the detrimental effects of metal impurity on the negative plate.

In another broad aspect, the present battery elements comprise the addition of macroporous additives to the active material present in the positive and/or negative plates in a lead acid battery. In a further preferred embodiment, the macroporous particles have a reduced affinity for bonding with the active material in the positive and negative plates. A further preferred embodiment are resilient porous organic polymers produced by the process of this invention.

Metal impurities can be introduced into the battery during the battery manufacturing process, particularly in the starting materials used for battery manufacture. Many of the metal impurities can exist in the anion or cation form

i.e. a negative or positive charge respectively in sulfate solutions such as that represented by sulfuric acid electrolyte. Depending on the molarity of the sulfuric acid electrolyte and the metal impurity, such 10cation/anion
5 forms can change as the molarity changes. Depending on such sulfuric acid molarity, it is believed that platinum, gold, thallium, nickel, cobalt, iron, copper, antimony, silver, bismuth and tin can exist as anions even though such
10 existence as anions may be weak or unstable. Further, such anion forms may predominant at the sulfuric acid electrolyte concentrations which exist after battery charging. One of the particularly detrimental metal
impurities is platinum.

As set forth above, such metal impurities can be
15 introduced into the lead acid battery during manufacturing. In a number of battery designs, grid materials not having antimony as an alloying agent are used for battery manufacture. However, even in these types of batteries using nonantimony containing grids, antimony
20 can be introduced as an impurity in the starting materials for battery manufacture including the starting lead and leady oxide type materials.

Antimony which is present in the positive grid as an alloying agent can be oxidized and/or corroded to form a
25 soluble antimony ion which diffuses and/or migrates to the negative plate. Antimony at the negative plate can produce a number of detrimental problems such as self discharge and gassing particularly hydrogen formation. Antimony ion from the positive grid can exist in both the anion and cation
30 form, i.e. a negative or positive charge respectively. It is believed that the form of the anion or cation is dependent on the oxidation state of the antimony, i.e. +3 or +5, the

molarity of the sulfuric acid and the battery voltage. For example, it is believed that antimony can exist as SbO_2^+ cation and SbO_3^- anion in the antimony +5 state and as SbOSO_4^- , $\text{Sb}(\text{SO}_4)^{2-}$ SbO_2 in the antimony +3 state. These +3 anion forms are believed to exist when the molarity of the sulfuric acid is greater than one but may not exist at the fully recharged battery voltage. In addition, it is believed that antimony may exist as Sb^{+3} or SbO^+ in the antimony +3 state again depending on molarity and battery voltage. As set forth above, the sulfuric acid electrolyte participates in the discharge reactions taking place in the lead acid battery. Thus, the wt% sulfuric acid can decrease from 30-40 wt% sulfuric acid to from 10-14 wt% sulfuric acid depending on the type of battery design and the initial sulfuric acid concentration in the electrolyte. The amount of sulfuric acid remaining will be dependent on the percent of discharge of the battery with less sulfuric acid remaining when batteries are discharged to 80% or more.

The organic polymers having functional groups with a preferential affinity for metal impurities in the anion or cation state inhibit the detrimental effects of soluble metal impurity on the negative plate. While the exact mechanism of inhibition is not known, it is believed that the metal impurity anion or cation is bound by the functional group such as by the anion replacing the anion present on the functional group in an anionic polymer or by a cation replacing the cation when the organic polymer contains cation functional groups. Although anion and/or cation replacement is believed to be one mechanism for inhibiting the adverse effects of metal impurity ions, metal impurities can also form complexes and/or be solvated to inhibit the detrimental effect of metal

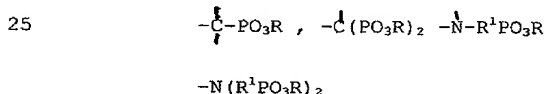
impurities on the negative plate and such mechanisms are included in then the term inhibiting. One of the major discoveries of the battery elements of this invention is the inhibition of metal impurities over the varying
5 sulfuric acid molarities and battery potentials (voltages) that occur during the charge discharge reactions in a lead acid battery. Further it has been discovered that the metal impurity which has been inhibited by the organic polymer additive is not substantially and detrimentally
10 desorbed and/or released from the polymer under the sulfuric acid molarity and battery voltage conditions and changes in a lead acid battery, that is the metal impurity inhibition continues during a plurality of charge/discharge reactions within the battery.

15 As set forth above, the organic polymers containing functional groups can introduce cations and/or anions into the battery element which cations or anions can be displaced by the metal impurity anion and/or cation. Further, the affinity of the organic polymer having such
20 metal impurity inhibiting functional groups have a stronger binding and/or complex formation and/or solvation of metal impurity ions when compared to any intermediate soluble lead ions such as lead +2 which may be formed during the conversion of solid lead, solid lead peroxide
25 to insoluble lead sulfate. As is known by those having skill within the lead acid battery art, cations and/or anions which are displaced by metal impurity cations or anions should not introduce any substantial detrimental effects on battery performance.

30 As set forth above, one of the classes of organic polymers has functionality which have affinity for metal impurity in the cation form. The metal impurity cation

displaces the cation associated with the functional group, Typically, the cation displaced can be hydrogen ion or, for example, sodium ion. The organic polymers having such cation functionality can be further classified as strongly
 5 acidic cation polymers or weakly acidic cation polymers. Particularly preferred strongly acidic cation polymers are those containing sulfonic acid groups or their sodium salt i.e. sulfonic groups preferably in the hydrogen form. Typical examples of polymers containing the sulfonic acid
 10 and/or sulfonate functionality are those derived from polystyrene crosslinked divinylbenzene, phenol-formaldehyde polymers and other like aromatic containing polymers.

As set forth above the organic polymer can have
 15 different functional groups such as functional groups containing strongly acidic functionality such as sulphonic and phosphonic functionality on the same organic polymer. As set forth above, strongly acidic cation polymers are preferred for inhibiting the effects of metal impurities.
 20 A particularly preferred functionality on the polymer is phosphonic acid and/or phosphonate here in after referred to as phosphonic functionality. Typical examples of such functionality are:



where R is typically hydrogen or sodium ion, preferably
 30 hydrogen and R¹ is alkylene, preferably methylene.

In general the phosphonic functionality can be incorporated into the polymer matrix by chemical reaction

including grafting of such functionality, of for example the aromatic portion of polystyrene and/or phenol-formaldehyde polymers. In addition, the functionality can be incorporated by the copolymerization of unsaturated vinylmono or gem phosphonic acid or ester monomers with other monomers particularly styrene, with still other monomers such as acrylate or acrylonitrile together with a cross-linking agent such as divinylbenzene. A typical monomer used for such copolymerization is vinylidene diphosphonic acid or the ester thereof to produce gem phosphonic functionality. Further examples of such polymers are polymers having a plurality of amino alkylene, phosphonic acid or phosphonate associated with the organic polymer.

As set forth above bis-derivatives are also useful including imino-bis(methylenephosphonic acid). The particularly preferred functionality is amino methylenephosphonic acid groups on polystyrene cross-linked with divinylbenzene.

As set forth above, phosphonic functionality can be incorporated into the polymer by reaction with an existing polymer matrix or by copolymerization of for example a vinyl phosphonic monomer. A preferred polymer is one containing polymerized styrene monomer either as a homopolymer or as an inter polymer with other polymerized monomeric units. Such polymers containing polymerized styrene as one of the monomers are generally referred to as polystyrene polymers.

As set forth above the organic polymer can have different functional groups such as functional groups containing strongly acidic functionality such as sulphonic and phosphonic functionality on the same organic polymer.

The organic polymers having phosphonic functionality can be combined with at least one component of an expander in the negative active material to provide improved maintenance of the lead acid batteries. Typical examples of the organic polymers having phosphonic functionality are set forth above.

The weakly acidic cation polymers in general have carboxylic functionality and/or the sodium salt associated with the organic polymer. Typical examples of such polymers are those derived from unsaturated carboxylic acids such as acrylic, methacrylic or maleic crosslinked with another monomer such as divinylbenzene or ethylene dimethacrylate. The preferred organic polymers containing cation functionality are the strongly acidic cation polymers having sulfonic acid functionality.

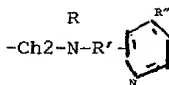
As set forth above, the organic polymer can have functionality having a preferential affinity for soluble metal impurity anions, i.e. the anion associated with the functionality is displaced by the soluble metal impurity anion in the electrolyte. The organic polymers having anion functionality can have both strongly basic and weakly basic anion functionality. Typical examples of strongly basic anion containing functionality are those having an ammonium functionality associated with the organic polymer. As set forth above, the anion associated with the functionality, typically sulfate or chloride, is displaced by the metal anion within the electrolyte. Typical ammonium groups associated with the polymer include trimethyl ammonium ion and dimethylethanol ammonium ion. Other groups include isothiuronium and derivatives thereof. Typical examples of organic polymers are polystyrene crosslinked with divinylbenzene. The ammonium ion with an appropriate anion

can be attached directly to, for example, the aromatic ring of the polystyrene or through, for example, a methylene bridge. Typical examples of weakly basic polymers having anion functionality are polymers which contain tertiary
5 aliphatic or aromatic aliphatic amine functionality's on the polymer such as polystyrene or a polyunsaturated carboxylic acids. Such polymers are typically crosslinked with a crosslinking agent such as the crosslinking agents referred to above. Further, the polymer basic anion
10 functionality can be obtained through aliphatic polyamine condensation reactions to produce the organic polymer. Typically, the weak base anion resins contain primary, secondary and/or tertiary amine groups generally as a mixture. Typical examples of such amine groups are
15 trimethyl amine and dimethylethanolamine. The preferred organic polymers having anion type functionality are the strongly basic anion containing functionality particularly for their strong binding and low release or desorption of metal impurity properties preferably having ammonium
20 functionality, particularly for incorporation into the negative plates. Since the electrolyte in the lead acid battery is sulfuric acid, it is preferred to use sulfate as the anion to be displaced by metal anion.

As set forth above the organic polymers can contain
25 primary, secondary or tertiary amine groups including aliphatic polyamine functionality. Further as set forth above, such organic polymers can contain aliphatic amine functionality. Further, as set forth above such polymers can contain amine functionality with acid functionality.
30 Particularly preferred functionality's associated with the organic polymer which contain both amine and acidic functionality are those containing secondary and tertiary

amine functionality and strong acid functionality, such as for example, the examples set forth above.

A particularly preferred class of aliphatic aromatic amine functionality are those having amino pyridine groups
5 associated with the organic polymer. Examples of such groups can be represented by the formula.



where in R is preferably an aliphatic substituent, an aliphatic polyamino substituent or a 2-picolene containing substituent, R' is preferably alkylene, preferably
10 methylene and R'' is a non-substantially interfering substituent, preferably hydrogen. Particularly preferred additives are organic polymers having functionality from 2-picolylamine, N-methyl-2-picolylamine, N-2hydroxyethyl)-2-picolylamine, N-(2-methylaminoethyl)-2-picolylamine and
15 bis-(2-picolyl)amine.

The aromatic aliphatic amine functionality's particularly the 2-picolylamine, such as bis-(2-picolyl)amine, are particularly useful in inhibiting the detrimental effects of copper and nickel.

20 As set forth above the organic polymers can contain primary, secondary or tertiary amine groups including aliphatic polyamine functionality. Further as set forth above, such organic polymers can contain aliphatic amine functionality. Further, as set forth above such polymers
25 can contain amine functionality with acid functionality. Particularly preferred functionality's associated with the organic polymer which contain both amine and acidic

functionality are those containing secondary and tertiary amine functionality and strong acid functionality, such as for example, the examples set forth above.

5 The organic polymers having functional groups with
affinity for metal impurity are typically within the
particle size ranges, porosity's, surface areas, additive
concentration and such other physical properties set forth
below with respect to porosity additives. The porosity of
10 the preferred organic polymers can vary over a wide range
such as within the ranges set forth below with respect to
micro and macro porosity. The porosity of the preferred
organic polymers is that which allows the metal impurity
ion, cation and/or anion to permeate the organic polymer
particle thereby affording good contact with the functional
15 groups attached to the external and internal surfaces of the
particles. The total displacement capacity of the organic
polymer having such functional groups is typically greater
than one milliequivalent of displaceable anion or cation per
gram of polymer, preferably greater than three and still
20 more preferably greater than five.

Any suitable positive active electrode material or
combination of such materials useful in lead-acid
batteries may be employed in the present invention. The
positive active electrode material can be prepared by
25 conventional processes. For example, a positive active
electrode material precursor paste of lead sulfate and
litharge (PbO) in water can be used, or conventional
pastes, such as those produced from leady oxide, sulfuric
acid and water, can be used. After the paste is applied to
30 the grid material, it is dried and cured. The precursor
paste may be converted to lead dioxide by applying a
charging potential to the paste.

Any suitable negative active electrode material useful in lead-acid batteries may be employed in the present invention. One particularly useful formed negative active electrode material comprises lead, e.g., sponge
5 lead. Conventional lead paste prepared from leady oxide, sulfuric acid, water and suitable expanders can be used. A suitable expander material typically comprises an organic expander, barium sulfate and carbon black. Typically, the organic expander is a purified product in the form of a
10 lignin sulfonic acid and is typically present at a concentration based upon the leady oxide used to form the active material of less than 2.0% typically less than 1.0 wt.%. The barium sulfate is typically a precipitated variety and is used as a lump-free powder having a particle
15 size less than 45 microns. The barium sulfate is typically used at a concentration of less than 0.5 wt.% basis the dry leady oxide used for the paste manufacture. Lastly, the carbon black is typically a finely divided carbon
20 black must be wettable by sulfuric acid electrolyte. Typically, the carbon black is used at a concentration of less than 0.5 wt.% basis the dry leady oxide. The concentration of the expander having all components is generally in the range of from 1 to 3 wt.% basis dry leady
25 oxide with the performance requirements of the battery being a factor in defining expander concentration in the negative plate.

Each of the cells of a lead acid battery further includes a non-electrically conductive separator acting to
30 separate the positive and negative electrodes of the cell and to hold electrolyte. Any suitable material may be used as a separator provided that it has no substantial

detrimental effect on the functioning of the cells or battery. Typical examples of separator material for batteries include glass fibre, sintered polyvinyl chloride and microporous polyethylene, which have very small pore sizes. Certain of these separators are formed as envelopes, with the pasted plates inside and the separator edges sealed permanently. Typically only the positive plates are encased in the separator. Separators uses for sealed lead-acid batteries operating on the oxygen recombination principle, i.e., oxygen recombinant batteries include one or more layers of silica-based glass, preferably separators formed of a highly absorptive porous mat of acid wettable binder free microfine glass fibers. Typically, a mix of fibers may be employed whose individual fibers have an average diameter in the range of about 0.2 to about 10 microns, more preferably about 0.4 to 5.0 microns, with possible minor amounts of larger gauge fibers to facilitate production of the mat. The porosity is preferably high, more preferably in the range of about 80% to about 98% and still more preferably about 85% to about 95%, if in the compressed state in the cell (slightly higher in the uncompressed state). The separator preferably has a relatively high surface area, more preferably in the range about 0.1 to about 20 m²/g, which facilitates the absorption and retention of relatively large amounts of acid electrolyte volumetrically while, if desired, still having a substantial unfilled pore volume permeable to oxygen for transport directly through the separator for consumption at the negative electrode. The particularly preferred separator materials have a surface area as measured by the BET method of in the range about 0.2 to about 3.0 m²/g., especially about 1.0 to about 2.0 m²/g.

As set forth above

As set forth above metal impurities are particularly detrimental in sealed lead acid batteries operating on the oxygen recombination principal, i.e. recombinant batteries. A number of impurity metals can exert a deleterious effect on the performance of recombinant batteries by for example, effecting one of more of the performance requirements of the recombinant batteries such as by increasing oxygen, evolution at the positive electrode, increasing hydrogen evolution at the negative electrode, inhibiting oxygen recombination at the negative electrode and in increasing the amount of water lost by the battery. Typical examples of metals that are particularly deleterious in recombinant batteries are arsenic, antimony, cobalt, chromium, nickel and tellurium.

As set forth above, the metal impurity inhibiting additives can be incorporated directly into the positive active material or negative active material for reducing the detrimental effects of the soluble metal impurity on the negative plates. Further, the metal impurity inhibiting additives, as set forth above, can be coated on the separator such as the glass fiber mats used in lead acid batteries. Further, the metal impurity inhibiting additives can be incorporated into the porous polymeric separators, such as polyvinyl chloride and microporous polyethylene. Typical concentrations of the additives associated with the separator is less than about 10 wt% preferably less than about 5 wt% basis the weight of the separators. The preferred metal impurity inhibiting additives are the porous organic polymers which allow for the inhibiting effect of the additives while not detrimentally adversely effecting the flow of electrolyte from and/or through the separator to the positive and negative plates.

In another broad aspect for manufacturing tin dioxide coated porous substrates, the process comprises contacting a porous substrate with a composition comprising a tin oxide precursor, such as tin chloride forming components, including stannic chloride, stannous chloride, tin complexes and mixtures thereof, preferably stannous chloride, at conditions, preferably substantially non-deleterious oxidizing conditions, more preferably in a substantially inert environment or atmosphere, effective to form a tin oxide precursor-containing coating, such as a stannous chloride-containing coating, on at least a portion of the substrate. The substrate is preferably also contacted with at least one dopant-forming component, such as at least one fluorine component, at conditions, preferably substantially non-deleterious oxidizing conditions, more preferably in a substantially inert atmosphere, effective to form a dopant-forming component-containing coating, on at least a portion of the substrate. The coated porous particles are particularly useful in a number of applications, particularly lead acid batteries, for example, monopolar and bipolar batteries, catalyst, resistance heating elements, electrostatic dissipation elements, electromagnetic interference shielding elements, electrostatic bleed elements, protective coatings, field dependent fluids and the like. In practice the particles which are preferred for use in such applications in general have an average length in the range of from about 20 microns to about 7 mm and an average thickness in the range of from about 20 microns to about 7 mm, the average length and thickness being different or the same depending on particle geometry and application. As set forth above, the

FIG 810-6

substrate can be optimized for a particular application and the particular electrical and/or mechanical requirements associated with such end use application. For example, in applications in which the particles are combined with other materials, such as polymers and positive active material of a lead acid battery and depending on the requirements of the application, ranges of from about 3 microns to about 300 microns, or even less than about 5 microns, typically ranges of from about 3 microns to about 150 microns or from about 5 microns to about 75 microns are useful. The porous inorganic substrates, can be characterized by bulk density (gm/cc) which is the weight or mass per unit volume considered only for the particle itself, i.e., includes the internal pore volume, surface area (M²/gm), total pore volume(cc(hg)/gm), pore size distribution and percent apparent porosity. In general, it is preferred that the bulk density be from about 3% to about 85% more preferably from about 10% to about 70%, more preferably, from about 10% to about 60% of the true density of the substrate material. Bulk densities less than about 5% are also useful. In addition, the porous substrate can have a wide range of surface area (M²/gm) of from about 0.01 to about 700 preferably having a moderate to high surface area, preferably, from about 10 M²/gm to about 600 15 M²/gm, more preferably, from about 50 M²/gm to about 500 M²/gm.

The pore volume is preferably from about 0.4 cc/gm to about 3.5 cc/gm, or even up to about 5cc/gm, more preferably from about 0.7 cc/gm to about 4.5 cc/gm more preferably from about 0.7 cc/gm to about 3.25 cc/gm. The pore size distribution can vary over a wide range and can have various distributions including multi-modal, for example, bi-modal distribution of pores including macro pores

and micro pores. There ideally exists a relationship between pore diameter, surface area and pore volume, thus fixing any two variables generally determines the third. In general, the mean (50%) pore diameter for macro pores, i.e.,
5 generally classified as having a pore diameter greater than about 750 angstroms can vary from about 0.075 microns to about 150 microns, more preferably, from about 0.075 microns to about 10 microns. Micro porosity, generally classified as a porosity having a mean pore diameter of
10 less than about 750 angstroms can vary over a wide range. In general, the mean pore diameter for micro porosity can vary from about 20 angstroms to about 750 angstroms, more preferably, from about 70 angstroms to about 600 angstroms. The ratio of macro to micro porosity can vary over a wide
15 range and depending on the application, can be varied to provide optimized performance as more fully set forth under the various applications. In general, the ratio of percent macro porosity to micro porosity expressed as that percent of the total porosity can vary from about 0% to about 95%,
20 more preferably, from about 5% to about 80% macro porosity and from about 100% to about 5%, more preferably from about 95% to about 20% micro porosity.

As set forth above, the porous substrate can be inorganic for example, carbon and carbide, i.e., silicon
25 carbide, sulfonated carbon and/or an inorganic oxide. Typical examples of inorganic oxides which are useful as substrates include for example, substrates containing one or more alumino silicate, silica, alumina, zirconia, magnesia, boria, phosphate, titania, ceria, thoria and the
30 like, as well as multi-oxide type supports such as alumina phosphorous oxide, silica alumina, zeolite modified inorganic oxides, e.g., silica alumina, perovskites,

Ba-61-CIP 6

spinel, aluminates, silicates, e.g., zirconium silicate, mixtures thereof and the like. A particularly unique porous substrate is diatomite, a sedimentary rock composed of skeletal remains of single cell aquatic plants called diatoms typically comprising a major amount of silica. Diatoms are unicellular plants of microscopic size. There are many varieties that live in both fresh water and salt water. The diatom extracts amorphous silica from the water building for itself what amounts to a strong shell with highly symmetrical perforations. Typically the cell walls exhibit lacework patterns of chambers and partitions, plates and apertures of great variety and complexity offering a wide selection of shapes. Since the total thickness of the cell wall is in the micron range, it results in an internal structure that is highly porous on a microscopic scale. Further, the actual solid portion of the substrate occupies only from about 10-30% of the apparent volume leaving a highly porous material for access to liquid. The mean pore size diameter can vary over a wide range and includes macroporosity of from about 0.075 microns to 10 microns with typical micron size ranges being from about 0.5 microns to about 5 microns. As set forth above, the diatomite is generally amorphous and can develop crystalline character during calcination treatment of the diatomite. For purposes of this invention, diatomite as produced or after subject to treatment such as calcination are included within the term diatomite.

As set forth above, porous substrate particles can be in many forms and shapes, especially shapes which are not flat surfaces, i.e., non line-of-site materials such as pellets, extrudates, beads, including spheres, flakes,

aggregates, rings, saddles, stars and the like. The percent apparent porosity, i.e., the volume of open pores expressed as a percentage of the external volume can vary over a wide range and in general, can vary from about 20% to about 92%, more preferably, from about 40% to about 90%. In practice, the bead particles, including spheres, which are preferred for use in certain applications in general have a roundness associated with such particles generally greater than about 70% still more preferably, greater than about 85% an still more preferably, greater than about 95%. The bead products of this invention offer particular advantages in many of such applications disclosed herein, including enhanced dispersion and rheology.

Acid resistant inorganic substrates, especially fibers, flakes, and glass fibers, are particularly useful substrates, when the substrate is to be used as a component of a battery, such as a lead-acid electrical energy storage battery.

The porous substrate for use in lead-acid batteries, because of availability, cost and performance considerations, generally comprises acid resistant glass, and/or ceramics more preferably in the form of particles, for example, fibers, and/or flakes, and/or beads including spheres and/or extrudates as noted above.

The solid substrates including organic polymers for use in lead-acid batteries are acid resistant. That is, the substrate exhibits some resistance to corrosion, erosion, oxidation and/or other forms of deterioration and/or degradation at the conditions present, e.g., at or near the positive plate, negative plate or positive or negative side of bipolar plates or separator, in a lead-acid battery. Thus, the substrate should itself have an

inherent degree of acid resistance. If the substrate is acid resistant, the physical integrity and electrical effectiveness of the whole present battery element, is better maintained with time relative to a substrate having
5 reduced acid resistance. If glass or ceramic is used as the substrate particle, it is preferred that the glass have an increased acid resistance relative to E-glass. Preferably, the acid resistant glass or ceramic substrate is at least as resistant as is C-or Tglass to the
10 conditions present in a lead-acid battery. Preferably the glass contains more than about 60% by weight of silica and less than about 35% by weight of alumina, and alkali and alkaline earth metal oxides.

As set forth above, one of the preferred applications
15 for use of the porous substrates is in lead acid batteries. Thus, the substrates can be added directly to the positive active material of a lead acid battery, i.e., the positive electrode to improve battery performance, particularly positive active material utilization efficiency. One
20 particular, unique aspect of the porous substrates is that the substrate is able to provide an internal reservoir for holding sulfuric acid electrolyte required for carrying out the electro-chemical reactions in the positive active material. More particularly, the porosity improves overall,
25 high rate performance of the positive active material, i.e. improved utilization efficiency at varying rates of discharge time, including high rates and at short discharge times.

As set forth above, the physical properties of the
30 porous substrates can vary widely. It is preferred that the substrate have sufficient macro porosity and percent apparent porosity to allow for the utilization of the

78-55-012 b

electrolyte sulfuric acid contained in the pores during discharge of the positive active material and, in addition, that the bulk density be selected to reduce the overall weight of the positive active material while
5 enhancing the overall performance of the battery. In general, the preferable percent apparent porosity can vary from about 40% to about 92%, more preferably, from about 70% to about 90%. The preferred ratio of percent macro
10 porosity to percent micro porosity can vary over a wide range and in general is from about 20% to about 95% macro porosity, more preferably, from about 45% to about 90% macro porosity with the balance being micro porosity. The mean pore diameter, particularly mean macro pore diameter, can vary over a wide range with the utilization of electrolyte
15 during the condition of the discharge of the battery being an important factor i.e., at high rate discharges, such as cold cranking, high macroporosity is preferred. Preferred mean macro pore diameter is from about 1 micron to about 150 microns, more preferably, from about 5 to about 100 microns
20 or even from about 0.075 micron to about 10 micron and still more preferably from about 0.1 to about 5 microns .

As set forth above, a particularly preferred substrate is a porous particle, i.e. porous support, particularly beads, including spheres, extrudates,
25 pellets, rings, saddles, stars, etc., preferably within the bulk density, macro porosity, micro porosity, apparent percent porosity and surface areas as set forth above. The coated particles can provide improved performance in various applications, particularly, in the positive active
30 material of lead acid batteries. As set forth above, the porous substrate can provide a reservoir for electrolyte sulfuric acid which participates in the electrochemical

FIG. 5

reaction during discharge of the positive active material. A particularly unique embodiment of the present invention is the use of the porous substrate itself as an additive in the positive active material to provide a reservoir of electrolyte sulfuric acid while providing a light weight additive for incorporation into the positive active material. Such particles are porous and within the ranges as set forth above particularly the preferred ranges. Such porous substrates can be further coated with additional components such as with other surface components, which may improve recharge, i.e. oxidation as well as other conductive components. As set forth above, the porous substrate with or without an additional component provides unexpected improvement in the performance of the positive active material, particularly, in the high rate discharge conditions such as cold cranking under lower than ambient temperature conditions.

Another particularly unique embodiment of the present invention is the use of the porous substrate itself as an additive in the negative active material to provide a reservoir of electrolyte sulfuric acid while providing a lightweight additive for incorporation into the negative active material. Such particles are porous and within the ranges as set forth above for the porous substrates particularly the preferred ranges. Such porous substrates can be further coated with additional components such as other surface components which may improve recharge, discharge and/or overall life of the battery, such as conductive components which are stable at the conditions of the negative electrode such as carbon and conductive metals, which coated porous substrates are included within the scope of this invention and the term porous

substrate. The porous substrate with or without an additional component provides unexpected improvement in the performance of the negative active material particularly under cold cranking conditions particularly multiple cold cranking under lower than ambient temperature conditions. As set forth above, the porous substrate can provide unexpected improvement in cold cranking typically 0 degrees F or lower during a series of multiple cold cranking. In addition, the porous substrates in the negative active material can provide for improved active material surface area maintenance and active material morphology maintenance particularly at elevated temperatures such as from about 60-80 degrees C or higher.

Typically, the porous substrates with or without additional components are incorporated into the positive and negative active material typically at a concentration of up to about 5 wt%, typically up to about 3 wt% basis the active material.

As set forth above, it is preferred that the porous substrate particles have sufficient macroporosity and percent apparent porosity for the utilization of the electrolyte sulfuric acid contained in the pores during discharge of the active material. Further, as set forth above, the preferred mean macropore diameter is from about 0.075 microns to about 10 microns and still more preferably from about 0.1 to about 5 microns. Particularly preferred solid porous particles that exhibit sufficient macroporosity to allow for improved utilization of sulfuric acid electrolyte are silica containing inorganic oxides preferably diatomites particularly those as set forth above and organic based materials particularly polyolefins still more preferably polypropylene.

As set forth above the porous substrates are acid resistant and include a wide variety of materials, including inorganic and organic based materials. The porous substrates can be in a wide variety of shapes, including shapes that are reduced in size during the manufacture of the positive active material, such as in the blending and/or mixing of the porous substrate in positive active material manufacture. It is preferred that the resulting particles if reduced in size maintain porosity parameters within the ranges as set forth above. It is also preferred, that the particles have sufficient stiffness and or resistance to detrimental permanent deformation in order to maintain sufficient porosity for the sulfuric acid in the pores to participate in a number of repetitive discharge and charge cycles, such as greater than 50 cycles or even 100 cycles.

A further unique embodiment of the present invention is the use of a resilient organic porous substrate which resists detrimental permanent deformation, maintains sufficient porosity for the sulfuric acid in the pores, has resiliency to be deformed under the conditions of discharge particularly mechanical forces in the active material of the lead acid battery and has resiliency to approach or attain its original geometry upon recharge of the battery particularly an organic porous substrate and/or additive produced by the process of this invention. In a lead acid battery, the densities of the 30 active material change i.e. lead at a density of 11.34 gram/cc, lead peroxide at a density of 9.4 grams/cc, (negative and positive plate respectively) change during discharge of the battery to lead sulfate having a density

EXAMPLES

of 6.2 grams/cc i.e. lead sulfate. Upon recharge, the lead sulfate is converted back to lead and lead peroxide in the negative and positive plates respectively. The resilient organic porous substrates have the ability to be deformed during discharge and approach or attain their original geometry during recharge of the battery. The changes in density and the ability of the porous substrate to be deformed allows for increased availability and a greater amount of sulfuric acid from the pores of the substrate as a function of time to participate in a number of repetitive discharge and charge cycles leading to increased utilization efficiency. Typical examples of resilient organic porous substrates are elastomeric or rubber-like porous substrates wherein the pores allow the sulfuric acid to participate in discharge and charge cycles. Further examples of such organic resilient porous substrates are organic polymers including for example organic polymers selected from the group consisting of polyolefins, polyvinyl polymers, -phenol formaldehyde polymers, polyesters, polyvinylesters, cellulose and mixtures thereof. The polymers are selected to be acid resistant and compatible with the active material at the conditions of the electrode in which they are in contact. Various resilient organic porous substrates particularly porous particles can be produced using suspension polymerization of a dispersed phase consisting of monomers, cross-linking agents, initiators, i.e., catalysts and a co-solvent that functions to aid pore formation. The particle size, pore volume, pore size distribution and macroporosity can be varied within the ranges as set forth above. Such resilient organic porous substrates including particles as set forth above have

MM-65-CTP-5

geometry's and are typically used within the ranges as set forth above for the coated porous substrates, particularly the preferred ranges and, as set forth above, as to their use in positive active and negative
5 active material. Depending on the particular active material in which such resilient porous substrates are incorporated, such porous substrates can be further coated with additional components such as with other surface components which may improve overall properties such as
10 discharge, recharge and life of the active materials.

As set forth above, the porous substrates including resilient porous substrates can be incorporated into the positive and negative active material. The various porous substrates provide a reservoir of electrolyte sulfuric
15 acid in the active material. The reservoir of sulfuric acid in the porous substrates can be added to the porous substrate prior to the addition of the porous substrate to the positive and negative active material or incorporated into the porous substrate from the sulfuric acid
20 electrolyte present in the lead acid battery. Further, other liquids such as water can be substituted for sulfuric acid if a liquid is added to the porous substrate prior to the addition of the porous substrate to the active material. As is recognized by those of skill in the art,
25 only liquids which do not have an adverse detrimental effect on the performance of the battery should be added to the porous substrate prior to addition to the active material.

In a still further embodiment and as is set forth above, the porous substrate particles can be coated with
30 another material. One such material is a component which gives hydrophobic character to the porous substrate, i.e. the porous substrate with the component is not water wet

13-63-07705

to the same degree as without the component. Such change to hydrophobic character can enhance the flow of electrolyte within the active material by limiting the bonding of the active material to the pores present in the porous particles and to particle surfaces. A particularly preferred component is a silica based size having hydrophobic alkyl groups such as methyl, ethyl or isooctyl which provide for hydrophobic character on the surface of the porous particles. Many of the organic porous particles within the scope of this invention have inherent hydrophobic properties such as the polyolefins whereas other have a combination of hydrophilic and hydrophobic properties. As set forth above, it is preferred that the porous particles have sufficient hydrophobic character to reduce the permanent bonding of the active material to the surfaces of the porous particles particularly the pores of the particles. The reduced bonding of the active material to the porous particles allows for improved diffusion of the sulfuric acid electrolyte to the interior of the active material associated with the positive and/or negative plate.

As set forth above, the additives are typically incorporated into the positive and negative active material at a concentration of up to about 5 wt%. The porous particle additives and the antimony inhibiting additives are incorporated during battery manufacture preferably during the production of the paste prior to application on the grid material. The additives can be incorporated into, for example, the lead, leady oxide powders to which the sulfuric acid and water are added. Alternatively, the additives can be mixed into the precursor paste prior to applying on the grid material. It

is preferred that the additives be incorporated such as to provide a uniform distribution of the additive particles throughout the entire paste, active material.

- Further, the porous substrate as set forth above can
- 5 be an acid resistant organic material, including organic polymeric materials as set forth above. Preferred polymers are polyolefin polymers, polyvinyl polymers, phenolformaldehyde polymers, polyesters, polyvinylesters and mixtures thereof. Preferred polymers are polyolefins,
- 10 preferably polypropylene, phenolformaldehyde polymers and polyvinylester, particularly modacrylic polymers.

Certain of these and other aspects to the present invention are set forth in the following examples.

EXAMPLE 1

A negative plate battery element is manufactured from a commercial battery paste having a density of 4.2 grams/cc. A porous polypropylene polymer powder having an average diameter of less than 400 microns and having a void volume of approximately 50-80% outer pore dimensions of 1-10 microns and smaller near surface pore dimensions of 0.1 to 1 microns is reduced in size under low shear aqueous slurry conditions to a particle size distribution of from 20 to 150 microns. The additive is incorporated into a freshly prepared wet paste at a concentration of 1.00 wt% basis, the dry lead content of the paste prior to incorporation of the additive. The additive is combined with two times its weight of water to fill the pores of the additive prior to incorporation into the paste. The additive is distributed in the paste and pasted on a series of negative grids. The negative plates were cured and assembled into a 12-volt battery with 6% antimony grid positive plates, formed and tested. An improvement in utilization efficiency at a high discharge rate is obtained.

EXAMPLES 2 THROUGH 4

In the following examples, microporous polypropylene powders having particle sizes of less than 400 microns, less than 1,500 microns and a particle size range of 200-1,000 microns were processed to reduce the overall particle size below 150 microns. The polypropylene powders were added to a vacuum mixer with deionized water containing one part per hundred parts of a non-ionic surfactant (Nalco8801). The

water was added slowly with stirring while applying a vacuum typically 5-10 inches of mercury. The surfactant and vacuum aided in filling the internal pores of the polypropylene powders. It was estimated that the surfactant solution filled greater than 90% of the pore volume of the powders. The surfactant water solution was added until a powder aqueous slurry resulted as evidenced by the presence of external water to form the slurry. The powder aqueous slurries were then added to a machine manufactured by Urschel Laboratories, Inc. The Comitrol models had a center opening in which to feed the particle slurry and a second water particle free stream and an impeller which rotated at high speed forcing the slurry out to a stationary series of cutting surfaces arranged in a circular retaining device. It was estimated that for the 400 micron powder, the total solution, including both internal and external water was 95% with the remainder being 5% as dry powder. For the 1500 micron and 200-1000 microns powders, the total solution of the internal and external water was estimated to be 96% with the balance being 4% as dry powder.

EXAMPLE 2

The 400 micron powder slurry was fed into a Comitrol processor model 1700 with an impeller speed of 11,925 RPM. The cutting head was identified as 212084-1⁰. 1 1/2 lbs. of dry material in slurry form was fed into the rotating impeller at a time of approximately 5-10 seconds. The temperature in ^{was} use 70°F and out was 75°F. A product was recovered in which 64% of the product passed through 120 mesh sieve. The recovered material was recycled through the model 1700 but with a cutting head identified as 216084-1⁰. *He 12/5/03*

90% of the recovered product passed through 120 mesh. The temperature increased from 75°F in to 80°F out.

EXAMPLE 3

Example 2 was repeated except that the powder was 200-1000 microns and the cutting head was 190804-2°. The recovered product passed 100% through a 45 mesh sieve. The product was then processed through the same Comitrol model 1700 but with a cutting head identified as 212084-1°. 54% of the product passed through a 120 mesh sieve. This recovered product was again passed through the model 1700 using a cutting head identified as 216084-1°. 86% of the product passed through a 120 mesh sieve. The temperature from the initial pass to the final pass went from 70°F to 79°F. The total time slurry addition for the three passes was less than 30 seconds.

EXAMPLE 4

Example 3 was repeated except the polypropylene was less than 1500 microns. After three passes using the same sequence of cutting head as in Example 3, 89% of the product passed through a 120 mesh sieve.

While this invention has been described with respect to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.